

Chemistry and Analysis of Radionuclides

Laboratory Techniques and Methodology



Jukka Lehto and Xiaolin Hou

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The Authors

Prof. Jukka Lehto

University of Helsinki
Laboratory of Radiochemistry
A.I. Virtasen aukio 1
00014 Helsinki
Finland

Dr. Xiaolin Hou

Technical University of Denmark
Risø National Laboratory for Sustainable Energy
Radiation Research Division
Fredriksborgvej 399
4000 Roskilde
Danmark

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Preface

I started to give a lecture course on radionuclide analysis to students of radiochemistry in 2001. Two problems quickly became apparent. The first was that I could not properly lecture on this subject if the basic chemistry underlying the behavior of radionuclides in separation procedures was not understood. There seemed to be no sense in talking about precipitation of hydrolyzable metals with ferric hydroxide, for example, if the hydrolysis of metals was not understood. I had to go back to basics and teach the chemistry of the elements. This was a good choice – not least for myself – since I had to refresh my understanding of basic chemical phenomena. The second problem was that there was no adequate textbook on the chemistry of radionuclides. I had a handout from my predecessor to give to the students, but it had been written in the 1970s: it was good but outdated and short. Most books on radiochemistry available at that time, though comprehensive enough, contained little actual chemistry of the radionuclides and concentrated on their radioactive decay processes and the detection and measurement of radiation. In 2005 I began to write a text of my own, in Finnish. Then, seeing a broader need for such a text, I decided to write in English.

After working on the book for three years, I realized that analytical methods cannot be properly described if one has not done the analysis oneself, as was true in my case. I therefore asked Dr. Xiaolin Hou, of Risø National Laboratory, Denmark, to join me in the project. I knew him as a most experienced analytical radiochemist who had personally analyzed a great number of radionuclides in environmental and nuclear waste samples and developed new separation methods. During the past two years we have collaborated in writing this book, and I have learned a host of new things, not just from reading papers but also from extensive discussions with Dr. Hou.

Our book describes the basic chemistry needed to understand the behavior and analysis of radionuclides of most groups of elements, and the analytical methods required to separate the most important alpha- and beta- decaying radionuclides from environmental and nuclear waste samples (e.g., ^{90}Sr and plutonium isotopes). Many new radionuclides have become important in radiochemistry in the past ten to fifteen years. Most of these are very long-lived, appearing in spent nuclear fuel and

nuclear reactor structures and are relevant to safety analysis of the final disposal of the nuclear fuel and decommissioning waste. Mass spectrometric techniques are well suited for the measurement of these radionuclides (^{135}Cs , ^{129}I , etc.) because of their low specific activities. Traditionally, radiometric methods have been used to measure radionuclides, but the development of mass spectrometric techniques has opened up new avenues for the analysis of radionuclides, in particular for their analysis in much lower concentrations. Mass spectrometric measurements also create new requirements for radionuclide analyses, because the interfering radionuclides and other elements which need to be separated before measurement are mostly not the same ones that affect radiometric measurements.

My first intention was to write a book for undergraduate and post-graduate students, but now that the book is finished I see that it could also serve as a handbook for more experienced radiochemists – at least I hope so.

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Jukka Lehto
Professor in Radiochemistry
University of Helsinki
Department of Chemistry
Finland

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1

Radionuclides and their Radiometric Measurement

1.1

Radionuclides

The first radioactive elements – radium and polonium – were discovered by Marie Curie at the end of the nineteenth century. During the first decades of the twentieth century, tens of natural radioactive elements and their various isotopes in the uranium and thorium decay chains were identified. The first artificial radionuclide, ^{30}P , was produced by Frédéric and Irène Joliot-Curie in an accelerator by bombarding aluminum with protons. Today, more than two thousand artificial radionuclides have been produced and identified, especially after the discovery and use of nuclear fission of uranium and plutonium. This book focuses on radionuclides found in the environment and in nuclear waste. This chapter presents an overview of radionuclides, radioactive decay processes, and the radiometric measurement of radionuclides, which are categorized according to their sources and ways of formation; in later chapters they are classified based on their chemical nature and are discussed in more detail. Radionuclides can be primarily categorized into natural and artificial radionuclides.

1.1.1

Natural Radionuclides

In nature there are three types of radionuclides: those belonging to the decay chains of uranium and thorium, single very long-lived radionuclides, and cosmogenic radionuclides.

The decay chains of uranium and thorium start with two isotopes of uranium and one of thorium, ^{235}U , ^{238}U , and ^{232}Th , which were formed at the birth of the Universe some 13.7 billion years ago, and, since they are so long-lived, they have survived in the earth since its birth 4.5 billion years ago. These three primordial radionuclides each initiate a decay chain leading to the stable lead isotopes ^{207}Pb , ^{206}Pb , and ^{208}Pb , respectively. In between, there are altogether 42 radionuclides of 13 elements, of which nine elements, those heavier than bismuth, have no stable isotopes at all. The three decay chains are depicted in Tables 1.1–1.3. The determination of radionuclides

Table 1.1 Uranium decay chain.

Nuclide	Decay mode	Half-life	Decay energy (MeV)	Decay product
^{238}U	α	4.4×10^9 y	4.270	^{234}Th
^{234}Th	β^-	24 d	0.273	^{234}Pa
^{234}Pa	β^-	6.7 h	2.197	^{234}U
^{234}U	α	245 500 y	4.859	^{230}Th
^{230}Th	α	75 380 y	4.770	^{226}Ra
^{226}Ra	α	1602 y	4.871	^{222}Rn
^{222}Rn	α	3.8 d	5.590	^{218}Po
^{218}Po	α 99.98%	3.1 min	6.874	^{214}Pb
	β^- 0.02%		2.883	^{218}At
^{218}At	α 99.90%	1.5 s	6.874	^{214}Bi
	β^- 0.10%		2.883	^{218}Rn
^{218}Rn	α	35 ms	7.263	^{214}Po
^{214}Pb	β^-	27 min	1.024	^{214}Bi
^{214}Bi	β^- 99.98%	20 min	3.272	^{214}Po
	α 0.02%		5.617	^{210}Tl
^{214}Po	α	0.16 ms	7.883	^{210}Pb
^{210}Tl	β^-	1.3 min	5.484	^{210}Pb
^{210}Pb	β^-	22.3 y	0.064	^{210}Bi
^{210}Bi	β^- 99.99987%	5.0 d	1.426	^{210}Po
	α 0.00013%		5.982	^{206}Tl
^{210}Po	α	138 d	5.407	^{206}Pb
^{206}Tl	β^-	4.2 min	1.533	^{206}Pb
^{206}Pb		stable		

Table 1.2 Actinium decay chain.

Nuclide	Decay mode	Half-life	Decay energy (MeV)	Decay product
^{235}U	α	7.1×10^8 y	4.678	^{231}Th
^{231}Th	β^-	26 h	0.391	^{231}Pa
^{231}Pa	α	32,760 y	5.150	^{227}Ac
^{227}Ac	β^- 98.62%	22 y	0.045	^{227}Th
	α 1.38%		5.042	^{223}Fr
^{227}Th	α	19 d	6.147	^{223}Ra
^{223}Fr	β^-	22 min	1.149	^{223}Ra
^{223}Ra	α	11 d	5.979	^{219}Rn
^{219}Rn	α	4.0 s	6.946	^{215}Po
^{215}Po	α 99.99977%	1.8 ms	7.527	^{211}Pb
	β^- 0.00023%		0.715	^{215}At
^{215}At	α	0.1 ms	8.178	^{211}Bi
^{211}Pb	β^-	36 min	1.367	^{211}Bi
^{211}Bi	α 99.724%	2.1 min	6.751	^{207}Tl
	β^- 0.276%		0.575	^{211}Po
^{211}Po	α	516 ms	7.595	^{207}Pb
^{207}Tl	β^-	4.8 min	1.418	^{207}Pb
^{207}Pb		stable		

Table 1.3 Thorium decay chain.

Nuclide	Decay mode	Half-life	Decay energy (MeV)	Decay product
²³² Th	α	1.41×10^{10} y	4.081	²²⁸ Ra
²²⁸ Ra	β^-	5.8 y	0.046	²²⁸ Ac
²²⁸ Ac	β^-	6.3 h	2.124	²²⁸ Th
²²⁸ Th	α	1.9 y	5.520	²²⁴ Ra
²²⁴ Ra	α	3.6 d	5.789	²²⁰ Rn
²²⁰ Rn	α	56 s	6.404	²¹⁶ Po
²¹⁶ Po	α	0.15 s	6.906	²¹² Pb
²¹² Pb	β^-	10.6 h	0.570	²¹² Bi
²¹² Bi	β^- 64.06%	61 min	2.252	²¹² Po
	α 35.94%		6.208	²⁰⁸ Tl
²¹² Po	α	299 ns	8.955	²⁰⁸ Pb
²⁰⁸ Tl	β^-	3.1 min	4.999	²⁰⁸ Pb
²⁰⁸ Pb		stable		

in the decay chains has been, and still is, a major topic in analytical radiochemistry. They are alpha and beta emitters, most of which do not emit detectable gamma rays, and thus their determination requires radiochemical separations. This book examines the separations of the following radionuclides: U isotopes, ²³¹Pa, Th isotopes, ²²⁷Ac, ^{226,228}Ra, ²²²Rn, ²¹⁰Po, and ²¹⁰Pb.

In addition to ²³⁵U, ²³⁸U, and ²³²Th, there are several single very long-lived primordial radionuclides (Table 1.4) which were formed in the same cosmic processes as those that formed uranium and thorium. The most important of these, with respect to the radiation dose to humans, is ⁴⁰K. However, as this emits readily detectable gamma rays and does not require radiochemical separations, neither this nor the others are discussed further in this book.

The third class of natural radionuclides comprises cosmogenic radionuclides, which are formed in the atmosphere in nuclear reactions due to cosmic radiation (Table 1.5). These radionuclides are isotopes of lighter elements, and their half-lives vary greatly. The primary components of cosmic radiation are high-energy alpha particles and protons, which induce nuclear reactions when they impact on the nuclei of the atmospheric atoms. Most of the cosmogenic radionuclides are attached to aerosol particles and are deposited on the ground. Some, however, are gaseous, such as ¹⁴C (as carbon dioxide) and ³⁹Ar (a noble gas), and thus stay in the atmosphere. In

Table 1.4 Some single primordial radionuclides.

Nuclide	Isotopic abundance (%)	Decay mode	Half-life (y)
⁴⁰ K	0.0117	β^-	1.26×10^9
⁸⁷ Rb	27.83	β^-	4.88×10^{10}
¹²³ Te	0.905	EC	1.3×10^{13}
¹⁴⁴ Nd	23.80	α	2.1×10^{15}
¹⁷⁴ Hf	0.162	α	2×10^{15}

Table 1.5 Some important cosmogenic radionuclides.

Nuclide	Half-life (y)	Decay mode	Nuclide	Half-life (y)	Decay mode
^3H	12.3	beta	^7Be	0.15	EC
^{10}Be	2.5×10^6	beta	^{14}C	5730	beta
^{22}Na	2.62	EC	^{26}Al	7.4×10^5	EC
^{32}Si	710	beta	^{32}P	0.038	beta
^{33}P	0.067	beta	^{35}S	0.24	beta
^{36}Cl	3.1×10^5	beta/EC	^{39}Ar	269	beta
^{41}Ca	3.8×10^6	EC	^{129}I	1.57×10^7	beta

primary nuclear reactions, neutrons are also produced, and these induce further nuclear reactions. Two important radionuclides are produced in these neutron-induced reactions: ^3H and ^{14}C (reactions 1.1 and 1.2), whose chemistry and radiochemical separations are described in Chapter 13. These radionuclides – tritium and radiocarbon – are generated not only by cosmic radiation but also in other neutron activation processes in nuclear explosions and in matter surrounding nuclear reactors.



1.1.2

Artificial Radionuclides

Artificial radionuclides form the largest group of radionuclides, comprising more than two thousand nuclides produced since the 1930s. The sources of artificial radionuclides are:

- nuclear weapons production and explosions;
- nuclear energy production;
- radionuclide production by reactors and accelerators.

A wide range of radionuclides are produced in nuclear weapons production, where plutonium is produced by the irradiation of uranium in reactors and in nuclear power reactors. Most are *fission products*, and are generated by the neutron-induced fission of ^{235}U and ^{239}Pu . In nuclear power reactors, they are practically all retained in the nuclear fuel; however, in nuclear explosions they end up in the environment – on the ground in atmospheric explosions or in the geosphere in underground explosions. The spent nuclear fuel from power reactors is stored in disposal repositories deep underground. The radionuclide composition of nuclear explosions and the spent fuel from nuclear power reactors differ somewhat for several reasons. Firstly, the fissions in a reactor are mostly caused by thermal neutrons, while in a bomb fast neutrons are

mostly responsible for the fission events, and this results in differences in the radionuclide composition. Secondly, fission is instantaneous in a bomb, while in a reactor the fuel is irradiated for some years. This allows the ingrowth of some activation products, such as ^{134}Cs , that do not exist in weapons fallout. ^{90}Sr and ^{137}Cs are the most important fission products because of their relatively long half-lives and high fission yields. In addition to these, there is range of long-lived fission products, such as ^{79}Se , ^{99}Tc , ^{126}Sn , ^{129}I , ^{135}Cs , and ^{151}Sm , the radiochemistry of which is discussed in this book.

Along with fission products, activation products are also formed in side reactions accompanying the neutron irradiation. The intensive neutron flux generated in the fission induces activation reactions both in the fuel or weapons material and in the surrounding material. These can be divided into two categories, the first comprising the transuranium elements – a very important class of radionuclides in radiochemistry. These are created by successive neutron activation and beta decay processes starting from ^{238}U or ^{239}Pu (Figure 1.1). Of these, the most important and the most radiotoxic nuclides are ^{237}Np , $^{238,239,240,241}\text{Pu}$, $^{241,243}\text{Am}$, and $^{243,244,245}\text{Cm}$, which are discussed further in this book. In addition to transuranium elements, a new uranium isotope ^{236}U is also formed in neutron activation reactions.

Another activation product group comprises radioisotopes of various lighter elements. In addition to tritium and radiocarbon, a wide range of these activation products are formed in nuclear explosions and especially in nuclear reactors. Elements of the reactor's construction materials, especially the cladding and other metal parts surrounding the nuclear fuel, the steel of the pressure vessel and the shielding concrete structures are activated in the neutron flux from the fuel. Part of these activation products, such as elements released from the steel by corrosion, end up in the nuclear waste disposed of during the use of the reactor. A larger part,

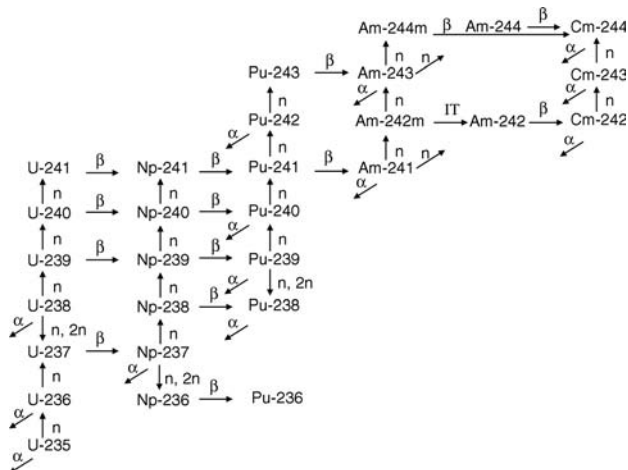


Figure 1.1 Formation of transuranium elements in nuclear fuel and nuclear weapons material (Holm, E., Rioseco, J., and Petterson, H. (1992) Fallout of transuranium elements following the Chernobyl accident. *J. Radioanal. Nucl. Chem. Articles*, **156**, 183).

however, remains in the steel and concrete and ends up in the waste when the reactor is decommissioned. This category has many important radionuclides, such as ^{14}C , ^{36}Cl , ^{41}Ca , ^{55}Fe , ^{59}Ni , and ^{63}Ni , which are discussed later in the book. These are all purely beta-decaying radionuclides that require radiochemical separations. In addition to these, there is a range of activation products, such as ^{60}Co , ^{54}Mn , ^{65}Zn , which emit gamma rays and are thus readily detectable and measurable. In addition to the reactor steel and shielding concrete, the spent fuel, its metal cladding, and other metal parts surrounding the fuel and ending up in the final disposal, contain large amounts of the long-lived beta decaying activation products ^{93}Zr , ^{94}Nb , and ^{93}Mo (together with ^{14}C , ^{36}Cl , ^{59}Ni , ^{63}Ni), which are also discussed in this book.

There are also a number of *radionuclides produced by neutron and proton irradiations in reactors and in cyclotrons*. Their properties are later described only if they are used as tracers in radionuclide analysis. An example is a fairly short-lived gamma-emitting strontium isotope, ^{85}Sr , which is used as a tracer in model experiments for studying the behavior of the beta-emitting fission product ^{90}Sr or as a yield-determinant in ^{90}Sr determinations.

1.2

Modes of Radioactive Decay

This book describes the chemistry and analysis of radionuclides – nuclei which are unstable, that is, radioactive. The instability comes from the fact that the mass of the nucleus is either too high or its neutron to proton ratio is inappropriate for stability. By radioactive decay, the nucleus disposes of the mass excess or adjusts the neutron to proton ratio more closely to what is required for stability. The four main radioactive decay modes – fission, alpha decay, beta decay and internal transition – are briefly described below.

1.2.1

Fission

Spontaneous fission is a characteristic radioactive decay mode only for the heaviest elements. In fission, the heavy nucleus divides into two nuclei of lighter elements which are called fission products. Of the naturally occurring isotopes, only ^{238}U decays by spontaneous fission. Only a very minor fraction, 0.005%, of ^{238}U decays by this mode, the rest decaying by alpha mode. Spontaneous fission becomes more prevailing with the heaviest elements, and for some, such as ^{260}No , it is the only way of decay. Considering the production and amounts of fission products, a more important process than spontaneous fission is induced fission: a heavy nucleus absorbs a particle, most usually a neutron, which results in the excitation and further fission of the nucleus (Figure 1.2). There are several fissionable isotopes, of which ^{235}U and ^{239}Pu are the most important from the point of view of the amounts of fission products generated. These two nuclides are not only fissionable but also fissile, that is, they undergo fission in the presence of thermal neutrons, which enables their use as

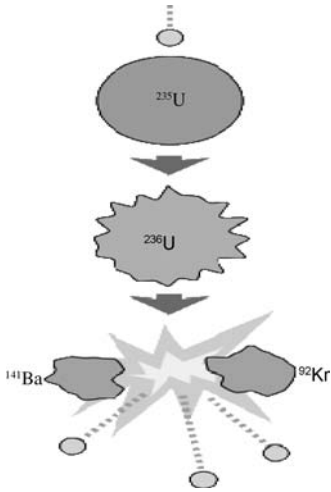


Figure 1.2 An example of a neutron-induced fission of ^{235}U . The reaction is $^{235}\text{U} + n \rightarrow ^{236}\text{U} \rightarrow ^{141}\text{Ba} + ^{92}\text{Kr} + 3n$ (http://en.wikipedia.org/wiki/Nuclear_fission).

nuclear fuel in nuclear reactors. ^{235}U is obtained by isotopic enrichment from natural uranium and ^{239}Pu by the irradiation of ^{238}U in a nuclear reactor and subsequent chemical separation of plutonium from the irradiated uranium.

A large number of fission products are generated in fission processes. Figure 1.3 gives, as an example, the distribution of fission products for ^{235}U from thermal

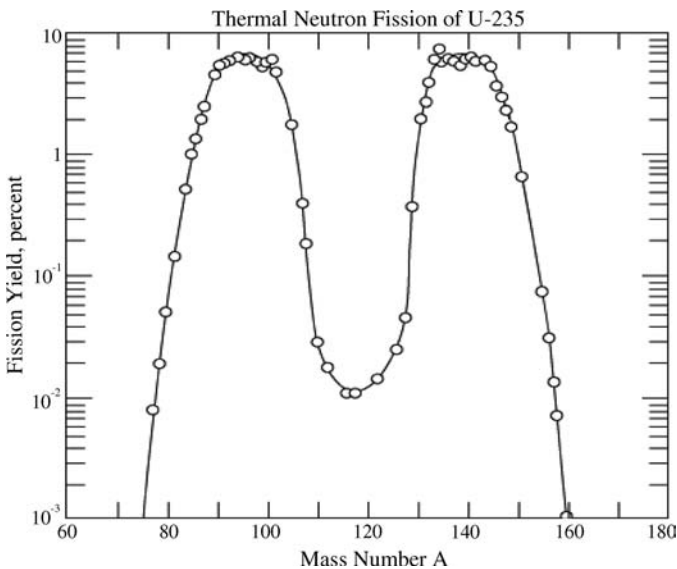
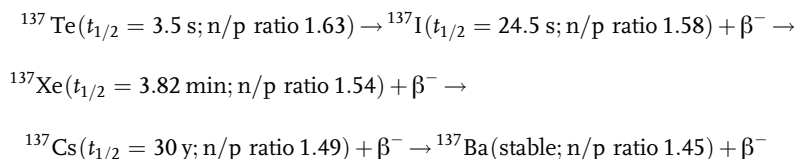


Figure 1.3 Fission yield distribution of ^{235}U as a function of the mass number of the fission product.

neutron-induced fission. As can be seen, the fission is extremely seldom symmetric, that is, the two fission products of one fission event are not of the same mass. Instead, the maxima of fission products are found at the mass numbers 90–100 and at 135–145. At these ranges, the fission yields are between 5% and 7%. This applies to thermal neutron-induced fission; fissions induced by high energy particles become more symmetric with the energy of the bombarding particle.

Most fission products are radioactive since they have an excess of neutrons. In both ^{235}U and ^{239}Pu , the neutron to proton ratio is around 1.6, which is too high for the lighter elements to be stable. For example, for the stable elements in the upper maximum of the fission yield at the mass numbers 135–145, the highest neutron-to-proton ratio is around 1.4, and, through the radioactive decay, by beta minus decay in this case, the nucleus transforms the ratio into an appropriate one. An example of such a decay chain of neutron-rich fission products leading to stable ^{137}Ba is as follows:



1.2.2

Alpha Decay

Alpha decay is also a typical decay mode for the heavier radionuclides. Most actinide isotopes and radionuclides in the uranium and thorium decay chains decay by this mode. A few exceptions among the radionuclides discussed in this book are ^{210}Pb , ^{228}Ra , and ^{241}Pu , which decay solely by beta emission. ^{227}Ac also decays mostly (98.8%) by beta decay. As can be seen from Tables 1.1–1.3, beta decay is a decay mode competing with alpha decay for many radionuclides in the decay chains. In an alpha decay, the heavy nucleus gets rid of excess mass by emitting a helium nucleus, which is called an alpha particle (α). An example is



where ^{226}Ra turns into ^{222}Rn by emitting an alpha particle. Thus, in an alpha decay, the atomic number decreases by two units and the mass number by four. The energies of the emitted alpha particles are always high, typically between 4 and 7 MeV. Since the mass of the alpha particle is relatively high, the daughter nuclide receives considerable kinetic energy due to recoil. For example, when ^{238}U decays to ^{234}Th by alpha emission, the daughter nuclide ^{234}Th gets 0.074 MeV of the 4.274 MeV decay energy and the alpha particle the rest, 4.202 MeV. Even though the fraction of the recoil energy is only 1.7%, this energy is some ten thousand times higher than that of a chemical bond, and thus recoil results in the breaking of the chemical bond by which the daughter nuclide is bound to the matrix. The transformations from parent nuclides to daughter nuclides take place between defined energy levels corresponding to defined